

特開昭61-271323 (2)

液)を溶解し、アノード化することを特徴とする導電性物質の製造方法である。

ここで、本発明における支持塩を含む溶液とは、過塩素酸テトラエチルアンモニウム、過塩素酸テトラブチルアンモニウム、四フッ化ホウ酸テトラエチルアンモニウム、四フッ化ホウ酸テトラブチルアンモニウム、六フッ化リン酸テトラエチルアンモニウム、六フッ化リン酸テトラブチルアンモニウム等のテトラアルキルアンモニウム塩、または、過塩素酸リチウム、四フッ化ホウ酸リチウム、六フッ化リン酸リチウム、過塩素酸ナトリウム等の電解質をニトロメタン、プロピレンカーボネート、テトラヒドロフラン、ジメチルフォルムアミド、γ-ブチロラクトン、シノトキレノタン、アセトニトリル、エトロベンゼン等の有機溶媒に溶解せしめたもの、或は、硫酸、過塩素酸水溶液等であり、特に好ましい組合せはテトラアルキルアンモニウム塩のニトロメタン溶液、または、過塩素酸水溶液である。支持塩(電解質)の濃度としては、0.1モル

/l~1モル/lの範囲が好ましく、フルオレンまたはその誘導体の濃度は0.01モル/l~10モル/lの範囲が好ましい。

本発明におけるアノード酸化のために使用する基種の導電性材料は、フルオレンまたはその誘導体の酸化電位よりも低い酸化電位を有するものであれば良い。

アノード酸化の方法は、定電流、定電位、または電位走査のいずれのものであっても良い。

本発明にて得られる導電性物質の電気伝導度の調節は、電析物の酸化の程度を変えることによって可能である。すなわち、生成した電析物(導電性物質)を、支持塩を含む溶液中ですらにアノード酸化するか、カソード還元することにより、電気伝導度をより大きくしたり、或はより小さくすることができる。

〔発明の作用・効果〕

本発明の導電性物質の製造方法によれば、電気伝導度を $10^{-7} \sim 10^0 (\Omega \cdot \text{cm})^{-1}$ の範囲で安定にして、かつ、制御可能な導電性物質が得ら

れるものである。

〔実施例〕

以下、本発明の実施例を示す。

実施例 1

10ccのエトロメタン中に過塩素酸テトラエチルアンモニウムを0.1モル/lの濃度で溶解し、更にこれにフルオレンを1モル/l溶解せしめた。この溶液中に1cm×1cmの白金板からなるアノードと1.5cm×2.0cmのニッケルメッシュ板からなるカソードとを所定間隔で対向して配置し、4mAの定電流通電を行った。

数十秒後に白金板は、電析物が付着して黒くなり始めた。1時間後白金板は、黒色析出物で完全に被覆された。この状態で通電を停止した。次いで、白金板を取り出しニトロメタンで洗淨後乾燥させた。乾後、白金板からフィルム状の析出物を剝離した。このフィルム状析出物の厚さは、0.1mmであった。このフィルム状析出物の電気伝導度を四端子法で測定したところ約 $0.6 (\Omega \cdot \text{cm})^{-1}$ であり、極めて安定しているこ

とが判った。

実施例 2

実施例 1と同様の条件で白金板上に電析物を得た後、この白金板を、過塩素酸リチウムを1モル/lの濃度でプロピレンカーボネートに溶解した電解質溶液中に電極として設置し、これにリチウム参照電極に対して2ボルトの定電位を24時間印加した。乾後、白金板から電析物を剝離して得たフィルム状析出物の電気伝導度を、実施例 1と同様に四端子法で測定したところ、約 $1.3 \times 10^{-7} (\Omega \cdot \text{cm})^{-1}$ であり、安定していることが判った。

実施例 3

10ccのエトロメタン中に過塩素酸テトラエチルアンモニウムを0.1モル/lの濃度で溶解し、更にこれに9-ヒドロキフルオレンを1モル/l溶解させた以外は実施例 1と同様にして、厚さ0.03mmのフィルム状析出物を得た。このフィルム状析出物の電気伝導度を実施例 1と同様に測定したところ、約 $0.8 (\Omega \cdot \text{cm})^{-1}$

特開昭61-271323 (3)

手続補正書

昭和 61.3.27

であり、安定していることが判った。

実施例4

過塩素酸テトラエチルアンモニウムを溶解したニトロメタン中に9-ヒドロキレフルオレンを1モル/1溶解させた以外は実施例2と同様にしてフィルム析出物を得た。フィルム析出物の厚さは約0.03mmであった。このフィルム析出物の電気伝導度を四端子法で測定したところ、約 $2.4 \times 10^{-1} (\Omega \cdot \text{cm})^{-1}$ であり、安定していることが判った。

特許庁長官 手 置 道 雄 殿

1. 事件の表示

特願昭60-113676号

2. 発明の名称

導電性物質の製造方法

3. 補正をする者

事件との関係 特許出願人

(529) 古河電気工業株式会社

4. 代理人

住所 東京都港区虎ノ門1丁目5番6号 第17層ビル
〒105 電話 03 (562) 3181 (大代表)

氏名 (5847) 弁護士 鈴 江 武 彦

5. 自発補正



6. 補正の対象

明 細 書



7. 補正の内容

- (1) 特許請求の範囲を別紙の通り訂正する。
 (2) 明細書、第2頁第18行目～第3頁第2行目に「本発明は、…製造方法」とあるのを下記のとおり訂正する。

記

「本発明は、支持塩を含む溶液中に、フルオレン  またはその誘導体  (ここで、XはOH、Br、Cl、NH₂、アルキル基の何れか一種)を溶解し、アノード酸化することを特徴とする導電性物質の製造方法」

2. 特許請求の範囲

支持塩を含む溶液中にフルオレン  またはその誘導体  (ここで、XはOH、Br、Cl、NH₂、アルキル基の何れか一種)を溶解し、アノード酸化することを特徴とする導電性物質の製造方法。

出願人代理人 弁護士 鈴 江 武 彦

Japan Patent Office (JP) Patent Application Publication

Patent Publication Journal (A) Sho 61-271323

Date of Publication: Showa 61(1986) Dec. 1

Name of Invention: Method for Preparing Conductive Materials

Application Number: Sho 60-113676

Patent Application: Sho 60(1985) May 27th

Inventor: Kenji Shinozaki

Address; _____

Inventor: Akio Nojiri

Address; _____

Inventor: Ikuo Tomizuka

Address; _____

Applicant: Koga Denki Kogyo Inc.

Address; _____

Representative: Takehiko Suzue, Patent Attorney, including two other people

Details

1. Name of Invention

Method of preparing a conductive material.

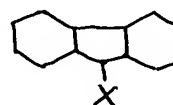
2. Range of Invention

Method of preparing a conductive material that features dissolving

Fluorene



or its derivative



(X is one kind selected from OH, Br, Cl, NH₂, and alkyl group) in a solution and making anode oxidation

3. Detailed Explanation of Invention

(Areas for Industrial usage)

This invention is about the method of preparing a conductive material.

(Current technologies and problems.)

Currently, polymer materials containing conjugated double bonds such as polyacetylene and poly-p-phenylene are known as organic materials that have high electric conductivity. However, polyacetylene is unstable and easy to get oxidized in the air. Although poly-p-phenylene is superior to polyacetylene in terms of stability, it is required to be doped with a material giving an electron or receiving an electron in order to improve electric conductivity. Consequently, the electric conductor that is thus obtained is unstable and its electric conductivity decreases with the passage of time.

Other than the organic materials mentioned above, polypyrrole, polythienylene, etc. are known as organic conductive materials. They also need to be doped with a material giving an electron or receiving an electron in order to improve its conductivity, and the electric conductors obtained by the doping are more stable than those shown above. However, such organic material as polypyrrole etc. also has a lot of room for improvement in terms of stability and strength. It has been desired to develop new conductive materials for improvement.

This invention has developed a method for preparing a conductive material that enables to regulate electric conductivity consistently within the range of $10^{-7} - 10^0$ (ohm \cdot cm)⁻¹.

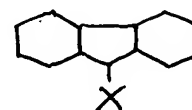
(Solutions to the problems)

This invention presents a method of preparing a conductive material that

features dissolving fluorene



or its derivative.



(X is one kind selected from OH, Br, Cl, NH₂, and alkyl group) in a solution and making anode oxidation.

In this invention, the solution that contains a salt includes an organic solvent such as nitromethane, propylene carbonate, tetrahydrofuran, dimethylformamide, α -butyrolactone, dimethoxyethane, acetonitrile, nitrobenzene etc. that dissolves an electrolyte such as tetraalkyl ammonium salts such as tetraethylammonium perchlorate, tetrabutylammonium perchlorate, tetraethylammonium tetrafluoroborate, tetrabutylammonium tetrafluoroborate, tetraethylammonium hexafluorophosphate, tetrabutylammonium hexafluorophosphate etc. or lithium perchlorate, lithium tetrafluoroborate, lithium hexafluorophosphate, sodium hexafluorophosphate; or aqueous sulfuric acid, perchloric acid etc. Preferable

combination is nitromethane and a tetraalkylammonium salt, or aqueous perchloric acid.

As for the concentration of the salt (electrolyte), the range from 0.1 mol/L to 1 mol/L is preferable. As for the concentration for fluorene or its derivative, the range from 0.01 mol/L to 1.0 mol/L is preferable.

As a conductive material of the electrode to be used for anode oxidation in this invention, it is fine as long as it has higher oxidation potential than that of fluorene or its derivative.

The method of anode oxidation may be a constant electric current method, constant potential method, or potential sweep method.

The control of the conductivity of the conductive materials obtained in this patent can be possible by changing the level of oxidation of the deposited material. In other words, it can make electric conductivity either smaller or bigger by making cathode reduction or anode oxidation of the formed conductive materials in the solution containing a salt.

(Function and Effectiveness of Invention)

According to the method of preparing a conductive material of this invention, the conductive materials that are stable and regulate conductivity within the range of 10^{-7} — 10^0 ($\text{ohm} \cdot \text{cm}$)⁻¹ can be obtained.

(Examples)

The below shows some examples for the present invention.

Example 1

Tetraethylammonium perchlorate was dissolved in 10 cc of nitromethane at the level of 0.1 mol/L, and then fluorene was dissolved in the nitromethane solution at the level of 1 mol/L. And in the solvent, an anode made of a 1 cm x 1 cm platinum plate and a cathode made of a 1.5 cm x 2.0 cm nickel mesh were set face to face at fix space and electric current of 4 mA was turned on through them.

Ten seconds later the platinum plate started to become black as a material was deposited on the plate. An hour later, the platinum plate was completely covered with the black deposits. Electric current was turned off under this condition. Next, the platinum plate was taken out, washed with nitromethane, and dried up. After that, the film-shaped deposits were torn off from the platinum plate. The thickness of the film-shaped deposits was 0.1 mm. When the conductivity of the film-shaped deposits was measured by the four-terminal method, it was about 0.6 ($\text{ohm} \cdot \text{cm}$)⁻¹. It was found to be very stable.

Example 2

Electrochemical deposits were obtained on the platinum plate under the same conditions as in Example 1. And then, the platinum plate having the deposits was set as an electrode in an electrolyte solution of propylene carbonate containing 1 mol/L of lithium perchlorate, and the platinum electrode was charged at a constant potential of 2 V against lithium as a reference electrode for 24 hours. After some time, the conductivity of the film-shaped deposits that were torn from the plate was measured by the four-terminal method in a similar manner as in Example 1. The conductivity was about $1.3 \times 10^{-6} (\text{ohm} \cdot \text{cm})^{-1}$. It was found to be stable.

Example 3

Film-shaped electrochemical deposits having a thickness of 0.03 mm were obtained in a similar manner as in Example 1 except that tetraethylammonium perchlorate was dissolved in 10 cc of nitromethane at the concentration of 0.1 mol/L and, in it, 9-hydroxyfluorene was dissolved at the concentration of 1 mol/L. The conductivity of the film-shaped deposits was measured by the same method as in Example 1. It was about $0.8 (\text{ohm} \cdot \text{cm})^{-1}$ and it was found to be stable.

Example 4

Film-shaped electrochemical deposits were obtained in a similar manner as in Example 2 except that 9-hydroxyfluorene was dissolved at the concentration of 1 mol/L in nitromethane in which tetraethylammonium perchlorate was dissolved. The thickness of the film-shaped electrochemical deposits was about 0.03 mm. When the conductivity of the film-shaped deposits was measured by the four-terminal method, it was about $2.4 \times 10^{-7} (\text{ohm} \cdot \text{cm})^{-1}$ and it was found to be stable.

Patent Application Rep: Takehiko Suzue, Patent Attorney

Correction

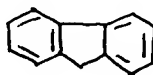
Showa 61 (1986), March 27

1. Indication of this matter
Tokugan Sho 60 —113676 (Application number)
2. Name of the invention
A method of preparing a conductive material.
3. Person who corrects and relationship with this matter
(529) Koga Denki Kogyo Inc., applicant
4. Representative
Takehiko Suzue, Patent attorney
Address;
5. Self-correction
6. Corrections: Details
7. Contents of corrections
 - (1) We correct the range of the patent request as shown in the attached page.
 - (2) "This invention is the manufacturing method" shown in from line 18 on page 2 to line 2 on page 3 in Detailed Explanation of Invention need to be corrected as indicated below.

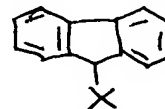
Note

This invention presents a method of preparing a conductive material that

features dissolving fluorene



or its derivative



(X is one kind selected from OH, Br, Cl, NH₂, and alkyl group) in a solution and making anode oxidation.

(A separate page)

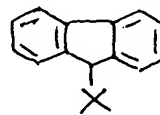
2. Range of Invention

Method of preparing a conductive material that features dissolving

fluorene



or its derivative



(X is one kind selected from OH, Br, Cl, NH₂, and alkyl group) in a solution and making anode oxidation

Representative: Takehiko Suzue, Patent Attorney